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Organorhenium Surface and Catalytic Chemistry: Silica-Supported Alkene Metathesis Catalysts Derived from Dodecacarbonyltetrakis(μ-hydrido)-*tetrahedro*-tetrarhenium and Tetrakis(tricarbonyl(μ_3-hydroxo)rhenium)

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Silica-supported $[Re(CO)_3OH]_4$ was formed by direct deposition from solution and, alternatively, by reaction of $[H_4Re_4(CO)_{12}]$ with adsorbed water, as shown by comparisons of infrared, ultraviolet, and ^1H NMR spectra of the surface and of the complex extracted into tetrahydrofuran. The supported $[Re(CO)_3OH]_4$ is inferred to be hydrogen bonded to surface –OH groups; its chemistry is similar to that of $[Re(CO)_3OH]_4$ in solution, but new reactivity is induced by the surface, with adsorbed $[HRe_3(CO)_{14}]$ being formed from $[Re(CO)_3OH]_4$ (or $[H_3Re_3(CO)_{12}]$) in the presence of CO at 150 °C. The supported $[Re(CO)_3OH]_4$ is the precursor of a highly active and stable catalyst for the metathesis of propene: the activity is associated with a small fraction of the rhenium in a higher oxidation state. The oxidation to form the active species takes place under conditions so mild that more highly oxidized species, which are active for alkene polymerization and coke formation, are not formed, and the catalyst is consequently resistant to deactivation.

Introduction

Most industrial catalysts are supported metals, metal oxides, or metal sulfides having nonuniform structures and poorly identified catalytic sites. Single crystals of metals and a few metal oxides have been used as structurally defined models of these catalysts; alternatively, structurally simple organometallics anchored to metal oxides have been suggested as models of supported catalysts. Metal carbonyl clusters have been used as precursors of catalysts for several reactions, including CO hydrogenation[1,2] and alkene hydrogenation and isomerization,[3,4] but the metals typically aggregate into crystallites, with the advantages of structural simplicity then being lost. Supported metal oxide clusters (heteropoly acids) have been investigated as selective oxidation catalysts, offering the prospects of much greater stability than the metal clusters, but the literature is still sparse.[5]

Among the many metal and metal oxide clusters available as precursors of supported catalysts, those incorporating rhenium are of particular interest because of rhenium's importance as a component of catalysts used for reforming of petroleum naphtha and metathesis of alkenes. The objectives of the research reported here were to investigate the synthesis, reactivity, and catalytic activity of surface species formed from molecular rhenium precursors.

A number of attempts to prepare unique metal oxide-supported metathesis catalysts have been reported.[6-9] The support has a dramatic effect on the catalytic properties; typically, catalytic activity increases with increasing Lewis acidity of the support. Alumina-supported rhenium catalysts are highly active even at room temperature,[10,11] but catalysts derived from Re_2O_7/SiO_2 are reportedly not active for propene metathesis even at 180 °C.[10] Silica-supported catalysts prepared from organorhenium compounds exhibited little or no activity; slightly active catalysts were generated by oxidation of these materials at 400 °C followed by reduction with hydrogen.[6]

In the following paragraphs, we describe the surface chemistry of $[Re(CO)_3OH]_4$ on silica and its preparation from $[H_4Re_4(CO)_{12}]$. Spectroscopic methods were applied to elucidate the structures and reactivities of the surface species prepared from $[H_4Re_4(CO)_{12}]$ and $[Re(CO)_3OH]_4$. The material is the first active and stable silica-supported rhenium catalyst for alkene metathesis.[12]

Results and Discussion

Synthesis of $[Re(CO)_3OH]_4/SiO_2$. Surface-bound rhenium complexes were prepared by refluxing an octane solution of the organometallic precursor ($[Re(CO)_3OH]_4$ or $[H_4Re_4(CO)_{12}]$) with hydrated silica for 4 h.[13] The infrared spectra of the resulting supported rhenium species are shown in Figure 1 with that of $[Re(CO)_3OH]_4$ in THF solution and those of solutions formed by the extraction of the supported complexes with THF. Except for a slight shift of the two bands and some broadening (typical of supported organometallics), the spectrum of the supported rhenium species is the same as that of $[Re(CO)_3OH]_4$ in solution, and evidently this complex could be extracted from the surface by THF. These results indicate that $[Re(CO)_3OH]_4$ was deposited directly on the surface and that $[Re(CO)_3OH]_4$ was formed on the surface when $[H_4Re_4(CO)_{12}]$ was brought in contact with it.

These inferences were confirmed by a comparison of the UV-visible spectra of the surface and molecular species (Figure 2). The spectra of the THF extracts are also shown in Figure 2, confirming that $[Re(CO)_3OH]_4$ was extracted by THF.

The surface ^1H NMR spectrum of a sample prepared from $[H_4Re_4(CO)_{12}]$ and silica showed a chemical shift of δ 5.9 (Figure 3), but this resonance cannot be unequivocally identified with the rhenium complex, since it could instead indicate surface hydroxyl groups (which typically lie at 0 ppm[14]) interacting with the rhenium complex. A solution spectrum of a methanol-d_4 extract of the sample yielded a value of δ 6.1, which is in agreement with the reported value of δ 6.12 for $[Re(CO)_3OH]_4$ in acetone-d_6,[15] confirming the inferences stated in the preceding paragraphs.

Extraction of $[Re(CO)_3OH]_4$ from the Support. $[Re(CO)_3OH]_4$ was recovered nearly quantitatively from the support when the samples were refluxed in THF for 5 h and then allowed to stand for 96 h at 25 °C. From the absorption at λ_{max} (280 nm), it was determined that 93% of the rhenium was recovered as $[Re(CO)_3OH]_4$ from the sample prepared from $[H_4Re_4(CO)_{12}]$. More than 96% of the $[Re(CO)_3OH]_4$ was regained from the silica that had been brought in contact with $[Re(CO)_3OH]_4$. Infrared and UV–visible spectra of the extract solutions indicated $[Re(CO)_3OH]_4$ as the only detectable species removed from the surface. Infrared spectra of the solids taken after the extraction showed only trace amounts of the $[Re(CO)_3OH]_4$ and THF.

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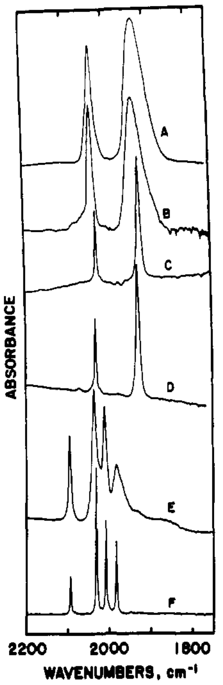

Figure 1. Infrared spectra: (A) $[H_4Re_4(CO)_{12}]$ (B) $[Re(CO)_3OH]_4$ supported on SiO_2; (C) THF extract of the $[H_4Re_4(CO)_{12}]$-derived surface complex; (D) $[Re(CO)_3OH]_4$ in THF; (E) $[H_3Re_3(CO)_{12}]$ adsorbed on SiO_2; (F) $[H_3Re_3(CO)_{12}]$ in cyclohexane. The absorption of the SiO_2 support was subtracted from spectra A, B, and E.

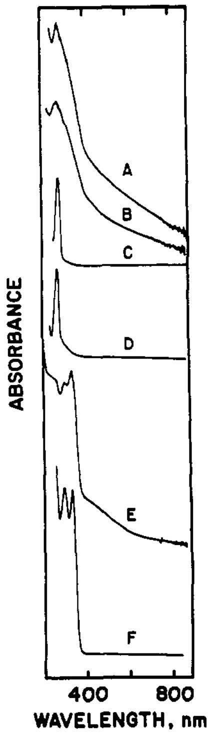

Figure 2. Electronic absorption spectra: (A) $[H_4Re_4(CO)_{12}]$ supported on SiO_2; (B) $[Re(CO)_3OH]_4$ supported on SiO_2; (C) THF extract of the $[H_4Re_4(CO)_{12}]$-derived surface complex; (D) $[Re(CO)_3OH]_4$ in THF; (E) $[H_3Re_3(CO)_{12}]$ adsorbed on SiO_2; (F) $[H_3Re_3(CO)_{12}]$ in cyclohexane. The absorption of SiO_2 was subtracted from spectra A, B, and E.

X-ray fluorescence analysis of the solids before and after extraction showed tha 13% of the original rhenium remained on the surface of the sample prepared from $[H_4Re_4(CO)_{12}]$ and 2% of the rhenium remained on the surface of the sample prepared from $[Re(CO)_3OH]_4$.

The behavior of the samples in the presence of other solvents provided a further indication of the reactivity of the surface species and a comparison with that of molecular analogues. When a sample was stirred in warm, dry methylene chloride or *n*-hexane for 24 h or allowed to stand in either of these solvents for 120 h, the solution infrared spectra remained unchanged, indicating that the surface complex had not been removed. Addition of small amounts of methanol or 2-propanol to the methylene chloride suspension led to the extraction of $[Re(CO)_3OH]_4$. Over long periods, alcohols attacked the complex, as evidenced by additional bands in the spectrum; however, as expected, addition of a quaternary ammonium salt stabilized the solvated species.[15]

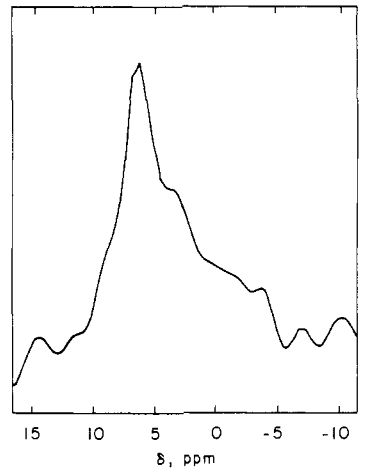

Figure 3. ^1H NMR spectra of the $[H_4Re_4(CO)_{12}]$-derived surface complex.

Only donor solvents are reported[15] to dissolve $[Re(CO)_3OH]_4$ and its halogen-substituted analogues $[Re(CO)_3X]_4$ (X = Cl, Br, I).[16,17] We infer, therefore, that the extractability of the silica-supported $[Re(CO)_3OH]_4$ is simply predicted by its solubility in the extract solvent. This result, combined with the spectral evidence that the complex interacts only weakly with the surface, suggests a weak acid–base interaction between the –OH groups of the complex and those of the silica surface. We suggest that the downfield shift in the infrared spectra of the extracted complex relative to those on the surface is an indication of more extensive hydrogen bonding in the solutions, which accounts for the removal of the rhenium complex from the surface.

Synthesis of $[H_3Re_3(CO)_{12}]/SiO_2$. $[H_3Re_3(CO)_{12}]$ was supported on SiO_2 by slurrying a hexane solution of the organometallic with silica at 25 °C. The close agreement between the infrared spectrum of the supported cluster and that of $[H_3Re_3(CO)_{12}]$ in cyclohexane (Figure 1) suggests that the intact cluster was present on the silica surface. Confirmation of this inference is provided by the comparison of the UV–visible spectrum of the supported cluster and that in solution (Figure 2).

Reactivity of Supported $[Re(CO)_3OH]_4$ with CO and O_2.[18] The chemistry of $[Re(CO)_3OH]_4/SiO_2$ in various environments was investigated with in situ infrared spectroscopy. Upon exposure of the supported complex to CO at 150 °C and 1 atm, spectrum A of Figure 4, which resembles that of $[HRe_3(CO)_{14}]$ (Table I), was observed. Removal of CO at 150 °C led to regeneration of the original spectrum (Figure 4E) with no loss in intensity, and the sequence could be repeated without any apparent loss of rhenium carbonyl. A similar spectrum, with the 1992-cm^{-1} peak resolved and indicative of $[HRe_3(CO)_{14}]$ (Figure 4B), was obtained when $[H_3Re_3(CO)_{12}]/SiO_2$ was subjected to CO under identical conditions.

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Scheme I

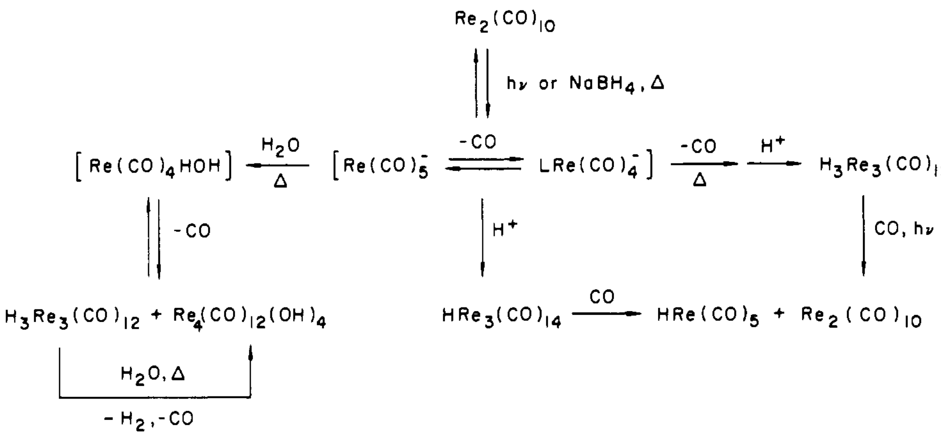

Table I. Infrared Stretching Frequencies of Rhenium Carbonyl Complexes

sample	ν(CO), cm^{-1}	ref
$[Re(CO)_3OH]_4$[a]	2021 s, 1919 vs	15
$[Re(CO)_3OH]_4/SiO_2$[b]	2032 s, 1930 vs	this work
$[H_3Re_3(CO)_{12}]$[c,d]	2093 m, 2030 vs, 2008 s, 1983 m	38
$[H_3Re_3(CO)_{12}]/SiO_2$	2095 m, 2035 vs, 2012 s, 1983 m	this work
$[HRe_3(CO)_{14}]$[c]	2143 vw, 2100 w, 2045 s, 2014 m, 1992 m (br), 1975 w, 1966 w, 1956 vw, 1936 w	19
$[HRe_3(CO)_{14}]/SiO_2$[e]	2095 w, 2053 s, 2017 m, 1995 m, 1990 m (sh), 1956 vw (sh)	this work
$[HRe_3(CO)_{14}]/SiO_2$[f]	2095 w, 2053 s (br), 1992 m (br), 1933 w	this work
$H_4Re_4(CO)_{12}]$[c]	2042 s, 1990 m	24

[a] In THF. [b] Both $[H_4Re_4(CO)_{12}]$- and $[Re(CO)_3OH]_4$-derived complexes. [c] In cyclohexane. [d] Principal absorptions. [e] from $[H_3Re_3(CO)_{12}]/SiO_2$. [f] From $[Re(CO)_3OH]_4/SiO_2$.

This surface chemistry can be rationalized on the basis of the reported solution chemistry of rhenium. It has been established that $[HRe_3(CO)_{14}]$ is an intermediate in the synthesis of $[H_3Re_3(CO)_{12}]$,[19] which occurs by reduction of $[Re_2(CO)_{10}]$ with $NaBH_4$, giving, most likely, mononuclear penta- and tetracarbonyl anions, with CO evolution. When this reaction is driven to completion by prolonged heating (so that only the tetracarbonyl anion is present), $[H_3Re_3(CO)_{12}]$ is obtained in good yield. However, if only partial CO dissociation occurs, then predominantly $[HRe_3(CO)_{14}]$ is found in the product mixture.[19] It has been demonstrated that both $[H_3Re_3(CO)_{12}]$[20] and $[HRe_3(CO)_{14}]$[19,21] react with CO to produce $[HRe(CO)_5]$ and $[Re_2(CO)_{10}]$. This chemistry is summarized in Scheme I, where the structures shown in brackets are presumed intermediates[15,19] and L represents a weakly bound ligand such as an oxygenated solvent.

Also shown in Scheme I is the synthetic route to $[Re(CO)_3OH]_4$, which presumably shares common intermediates with the pathway to the trirhenium clusters. This inference is supported by the observation of $[H_3Re_3(CO)_{12}]$ in the product mixture from the synthesis of $[Re(CO)_3OH]_4$. Heating the product mixture drives the homogeneous reaction to completion, and $[Re(CO)_3OH]_4$ is isolated in 98% yield.[15]

On the basis of this molecular chemistry, it is not surprising that when $[Re(CO)_3OH]_4/SiO_2$ is exposed to CO, the CO-rich intermediate in the synthetic route to $[H_3Re_3(CO)_{12}]$ is formed. Furthermore, we have demonstrated the transformation of $[H_3Re_3(CO)_{12}]$ to $[HRe_3(CO)_{14}]$ on the surface of silica. Consistent with the solution chemistry, when the time of reflux of $[H_4Re_4(CO)_{12}]$ with silica was reduced to 1 h, a spectrum (Figure 4D), having three additional bands (2094, 2008, 1980 cm^{-1}), was observed. These bands are assigned to $[H_3Re_3(CO)_{12}]$ (Table I); they disappeared when the sample was heated under helium at 150 °C.

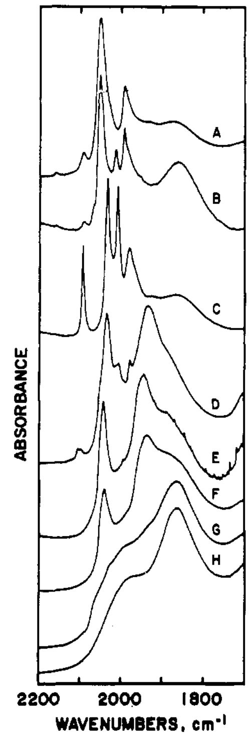

Figure 4. Infrared spectra: (A) $[H_4Re_4(CO)_{12}]$-derived surface complex after exposure to CO at 150 °C for 2 h; (B) $[H_3Re(CO)_{12}]$ on SiO_2 after exposure to CO at 150 °C for 4 h; (C) $[H_3Re_3(CO)_{12}]$ on SiO_2 as initially adsorbed; (D) $[H_4Re_4(CO)_{12}]$ on SiO_2 after 1 h in refluxing in *n*-octane; (E) $[H_4Re_4(CO)_{12}]$ on SiO_2 after 4 h in refluxing *n*-octane (standard preparation); (F) $[H_4Re_4(CO)_{12}]$-derived surface complex after exposure to flowing propene + He and He for 12 days; (G) $[H_4Re_4(CO)_{12}]$-derived surface complex after being held at 200 °C in He for 2 h; (H) pure SiO_2.

In summary, the foregoing results demonstrate strong similarities between the known solution chemistry and the surface chemistry of $[Re(CO)_3OH]_4$ and the related rhenium carbonyls. The surface chemistry is new and different in two important respects: (1) upon exposure of $[Re(CO)_3OH]_4$ to CO, $[HRe_3(CO)_{14}]$ can be reversibly generated, and (2) $[HRe_3(CO)_{14}]$ can be obtained from $[H_3Re_3(CO)_{12}]$ in the presence of CO. The latter result is in agreement with known chemistry in that $[HRe_3(CO)_{14}]$ is an intermediate product in the synthesis of $[H_3Re_3(CO)_{12}]$ (after CO dissociation); the differences between the surface and solution chemistry are the resistance of the trinuclear rhenium frameworks of $[H_3Re_3(CO)_{12}]$ and $[HRe_3(CO)_{14}]$ to fragmentation in the presence of CO and the apparent reversibility of the $[HRe_3(CO)_{14}]$–$[Re(CO)_3OH]_4$ transformation on the surface. We

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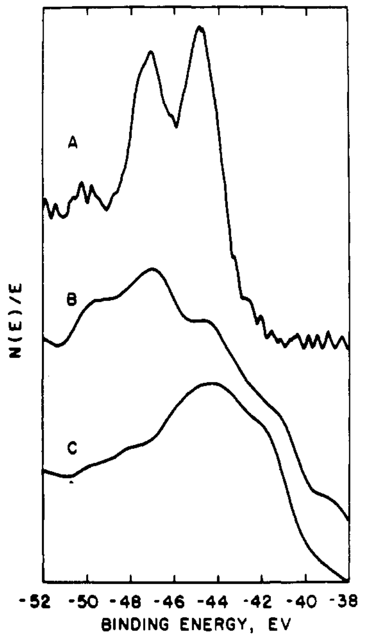

Figure 5. X-ray photoelectron spectra: (A) $[H_4Re_4(CO)_{12}]$ on SiO_2 (calcined at 700 °C), which had been held in refluxing dry *n*-octane for 4 h; (B) $[H_4Re_4(CO)_{12}]$-derived surface complex after 12 h at 250 °C in He (sample II); (C) $[H_4Re_4(CO)_{12}]$-derived surface complex (Sample I).

suggest that coordination of the rhenium to surface oxo, μ-oxo, and hydroxo ligands to prevent the formation of the volatile $[HRe(CO)_5]$ may be responsible for the novel reactivity and stability exhibited by the supported rhenium complexes.

The surface-bound $[Re(CO)_3OH]_4$, prepared either from $[H_4Re_4(CO)_{12}]$ or from $[Re(CO)_3OH]_4$ directly, was observed to be stable in air and under vacuum at room temperature. Heating the surface-bound $[Re(CO)_3OH]_4$ to 150 °C under He or vacuum for 24 h left the original infrared spectrum unchanged. Increasing the temperature to 200 °C resulted in decomposition of the complex (Figure 4) and total decarbonylation.[22]

Varying the water content of the silica used in the preparation of $[Re(CO)_3OH]_4$ had dramatic effects on the nature of the products. Use of uncalcined silica with *n*-octane (reagent grade) resulted in the formation of a species with an infrared spectrum indistinguishable from that obtained by using the standard preparation. In contrast, use of silica calcined at 400 °C with a solution of $[H_4Re_4(CO)_{12}]$ in *n*-octane dried over sodium yielded an unidentified solid having four bands in the carbonyl region of the infrared spectrum. Use of dry *n*-octane and silica that had been calcined for 12 h at 700 °C gave a light yellow solid with an infrared spectrum having no absorbances in the carbonyl stretching region. An X-ray photoelectron spectrum (Figure 5A) of this sample indicates the presence of Re^{6+}, which is indicative of ReO_3.[23]

Refluxing a solution of $[H_4Re_4(CO)_{12}]$ in *n*-octane with excess water in the absence of silica did not result in the formation of $[Re(CO)_3OH]_4$ in any measurable amount. We infer that both the silica surface and adsorbed water are necessary for the synthetic chemistry. The spectra indicate that water acts not only as a reactant but also to prevent further oxidation of the rhenium by the silica surface. In solution, $[H_4Re_4(CO)_{12}]$ reacts instantaneously with donor solvents,[24,25] leading to the formation of lower nuclearity carbonyls. Also, rhenium hydrides typically react with acids with complete displacement of the hydride ligands[26] and substitution of the conjugate base. To explain the conversion of $[H_4Re_4(CO)_{12}]$ into $[Re(CO)_3OH]_4$ on the surface, we suggest that $[H_4Re_4(CO)_{12}]$ fragments to give mononuclear carbonyl species, followed by reaction with water to form the hydroxorhenium tetramer; however, displacement of the hydride ligands with concomitant evolution of H_2 and the substitution of hydroxide to form $[Re(CO)_3OH]_4$ cannot be ruled out.[27] The observation that silica, which presumably aids cluster breakup, is necessary for reaction supports the former suggestion.

Table II. Activities of Catalysts for Propene Metathesis

sample	wt % Re	10^6 × reaction rate,[a] mol/g of Re·s	activation energy,[b] kJ/mol	ref
Re_2O_7/Al_2O_3[c]	8.3	1.1	39.6	10
Re_2O_7/Al_2O_3	8.3	420	46.0[d]	10
Re/SiO_2[e]	3.3	4.0	48.4[d]	this work
Re/SiO_2[f]	2.0	2.7		this work
Re_2O_7/Al_2O_3[g]	4.5	72	25.3	30
Re_2O_7/Al_2O_3[g]	4.5	73	40.6	30

[a] Normalized to 150 °C and a propene partial pressure of 0.6 atm. [b] For the disproportionation of propene to ethylene and but-2-ene. [c] For the metathesis of deuterated ethylene. [d] Apparent activation energy. [e] Sample I. [f] Sample II. [g] Same catalysts, different rate expressions.

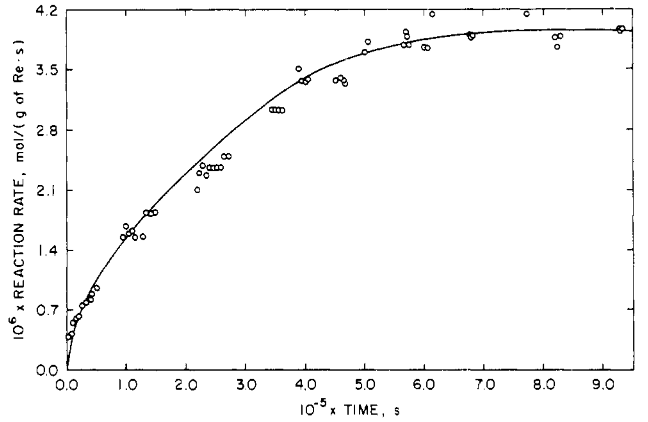

Figure 6. Changes in catalytic activity of sample I during alternating periods under propene + He and He at 150 °C and 1 atm.

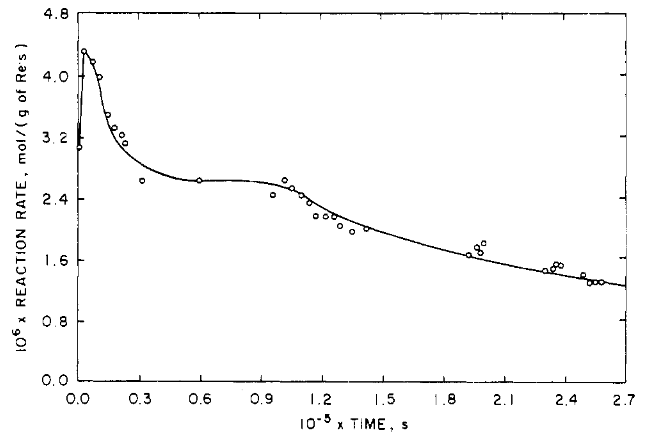

Figure 7. Changes in catalytic activity of sample II during alternating periods under propene + He and He at 150 °C and 1 atm.

Catalysis of Propene Metathesis: Activity and Stability. The samples prepared from $[H_4Re_4(CO)_{12}]$ supported on silica were found to be catalytically active for the metathesis of propene. Ethene and but-2-ene, produced in stoichiometric amounts, were

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(22) Pure $[Re(CO)_3OH]_4$ decomposes at 360 °C in air.

(23) Values of 40.6, 44.3, and 46.5 eV have been reported for the binding energies of the Re $4f_{7/2}$ peak of Re, ReO_3, and Re_2O_7, respectively: Shapiro, E. S.; Avaer, V. I.; Antoshin, G. V.; Ryashentseva, M. A.; Minachev, K. M. *J. Catal.* **1978**, *55*, 402.

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(27) The crystal structure of $[Re(CO)_3OH]_4$ can best be described as a distorted cube composed of two tetrahedra (Re, O) with a common center and no metal–metal bonds: Nuber, B.; Oberdorfer, F.; Ziegler, M. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 2062.

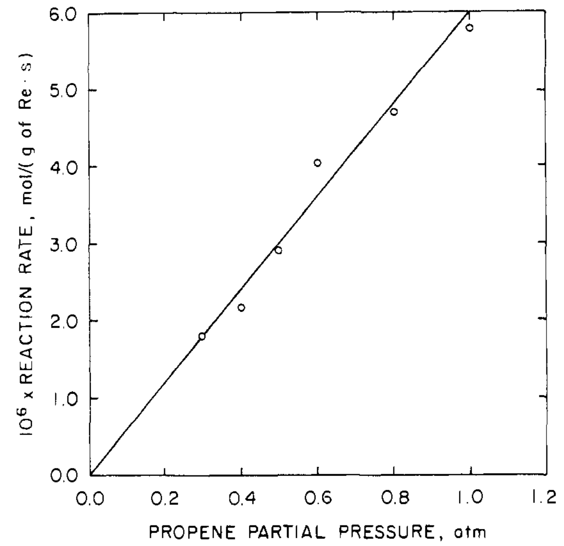

Figure 8. Effect of propene partial pressure on the rate of propene metathesis catalyzed by sample I at 150 °C and 1 atm.

the only observed products. Sample II (Table II) was prepared by pretreating the $[H_4Re_4(CO)_{12}]$-derived surface complex (i.e. sample I, Table II) in helium at 250 °C for 12 h. As demonstrated by the spectra of Figure 4, thermal activation at temperatures >200 °C led to cluster decomposition. Oxidation (presumably by surface –OH groups[3]) ensued, as shown by the shift to higher binding energy of the rhenium $4f_{7/2}$ peak in the X-ray photoelectron spectrum of the pretreated catalyst (Figure 5). These two catalysts were characterized in detail to evaluate the effect of oxidation on the catalytic properties.

The metathesis reaction rates observed with the two catalysts at steady state [Figure 6 (at 9.3×10^5 s) and Figure 7 (after 6.0×10^4 s)] are reported in Table II. The catalytic activities are about the same as those of the highly active Re_2O_7/Al_2O_3 catalyst (Table II). The stability exhibited by the untreated catalyst (sample I) is unique for a silica-supported rhenium catalyst; the extended activation period displayed by the supported organometallic is also unusual for a rhenium metathesis catalyst; short induction periods have, however, been observed for unpretreated catalysts.[11] The stability exhibited by the thermally activated $[H_4Re_4(CO)_{12}]$-derived catalyst (sample II) is similar to that of standard Re_2O_7/Al_2O_3 catalysts that have been pretreated with H_2 or olefin at temperatures >500 °C.[10]

An in situ infrared characterization of the unpretreated catalyst was performed under reaction conditions with a quartz cell as the catalytic reactor positioned directly in the infrared beam. The spectra obtained over a period of 36 h showed no change in the carbonyl region of the spectrum. However, an infrared spectrum of the catalyst removed from the conventional reactor after 12 days of operation (without exposure to air) showed that some cluster degradation had occurred, as demonstrated by the decrease in the principal bands of the cluster relative to that of silica at 1865 cm^{-1} (compare spectra E and F, Figure 4).

Catalytic Kinetics. The dependence of the reaction rates on propene partial pressure is shown in Figures 8 and 9.[28] The temperature dependence of the reaction rate for the unpretreated catalyst is shown in the Arrhenius plot of Figure 10. The apparent activation energy is 48.4 kJ/mol, which is in agreement with values reported for conventional alumina-supported rhenium catalysts (Table II).

The kinetics data for the two catalysts can be represented by a simple power-law rate expression

$$r = kP^n \tag{1}$$

Apparent orders in propene partial pressures, n, of 1.0 and 1.6

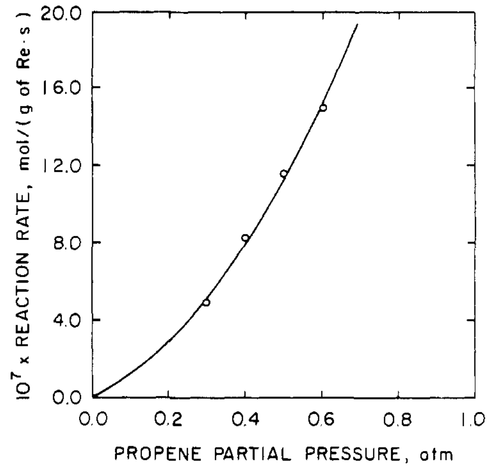

Figure 9. Effect of propene partial pressure on the rate of propene metathesis catalyzed by sample II at 150 °C and 1 atm.

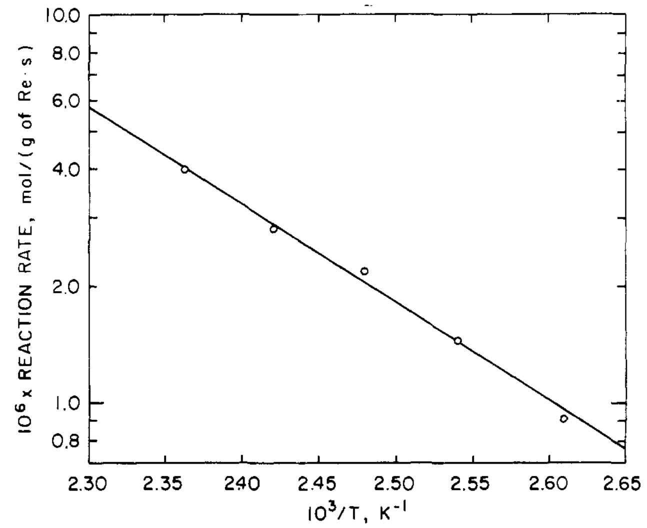

Figure 10. Arrhenius plot for propene metathesis catalyzed by sample I at 1 atm.

were obtained for the unpretreated and pretreated samples, respectively. Consistent with these results, Lin et al.[10] reported an intermediate value of 1.4 for the metathesis of propene catalyzed by Re_2O_7/Al_2O_3.[29]

The literature demonstrates that less than 1% of the rhenium atoms are active on standard alumina-supported catalysts.[11,30,31] The results of UV–visible, electron spin resonance, XP-spectroscopic, and detailed kinetics studies have led a number of authors to conclude that an intermediate oxidation state of rhenium (+2 or +4) is the active species on the alumina surface.[6,7,11,32,33] On the basis of the agreement between the activation energies and reaction rates characterizing our silica-supported catalysts and those characterizing conventional Re_2O_7/Al_2O_3, we suggest that similar species are catalytically active on both surfaces. In the unpretreated sample, the catalyst precursor is $[Re(CO)_3OH]_4$; we infer that this complex acts as a reservoir of rhenium, from which rhenium in an intermediate oxidation state is formed; this

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[28] Each point in Figures 7–9 represents the average of five experimental values.

[29] Both the observed reaction orders can be rationalized in terms of a carbene chain carrier mechanism involving surface methylidene and ethylidene complexes. A value of $n < 1$ can be derived by assuming that the concentration of the surface carbene complex at steady state is independent of alkene partial pressure. Adding the adsorption of propene on a metal center to form a carbene as a step in the reaction sequence can result in $n > 1$.

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latter species is then responsible for the metathesis. The activation of the catalyst under helium can be interpreted as an oxidation of a small amount of the organometallic by the surface hydroxyl groups, which are just becoming reactive at 150 °C. This inference is consistent with that reported for Re_2O_7/Al_2O_3 and is supported by the spectrum of the used catalyst (Figure 4F), which shows a decrease in the surface concentration of $[Re(CO)_3OH]_4$ after exposure of the sample to reaction conditions. The steady-state activity then presumably corresponds to an equilibrium between the supported organometallic and the oxidized rhenium species. In the pretreated sample (12 h; 250 °C under He), the predominant surface species is rhenium in a higher oxidation state; the catalyst is light blue, and the X-ray photoelectron spectrum suggests oxidation states of +6 and +7 (Figure 5). The literature interpretation for alumina-supported rhenium and the close agreement between the rates observed for the two silica-supported catalysts imply that the same rhenium species, existing in an intermediate oxidation state and present in small amounts, is a catalytically active species for metathesis on the pretreated catalyst.

When the pretreated catalyst was removed from the reactor, it was dark purple. When the unpretreated catalyst was removed, it was still light beige, the original color. The infrared spectrum of the used pretreated catalyst (held for 1 h at 10^{-4} torr to remove physisorbed species) showed absorbances in the C–H stretching region (2800–3000 cm^{-1}); no such absorbances were observed for the unpretreated catalyst. These results suggest that the color may be indicative of polyolefin on the surface, the formation of which is catalyzed by rhenium in a higher oxidation state; Re_2O_7/Al_2O_3 is known to be an active alkene polymerization catalyst.[31]

Exposure of Re_2O_7/SiO_2 to refluxing oct-1-ene has been reported[33] to result in the reduction of the rhenium to the +6 and +4 oxidation states, with rapid catalyst deactivation resulting from coke formation. Consistent with these reports, we suggest that our pretreated catalyst (incorporating Re^{+6} and Re^{+7}) suffers from deactivation caused by alkene polymerization and/or coke formation. In contrast, the unpretreated sample is much less subject to deactivation, with the predominant rhenium species, $[Re(CO)_3OH]_4$, acting as a stable reservoir of Re and not leading to deactivation of the catalyst.

Summary

The results demonstrate that the chemistry of rhenium carbonyls on silica can be largely accounted for on the basis of known solution chemistry, but the surface also opens up new chemistry. We suggest that a key to the surface chemistry is the stabilization of $[LRe(CO)_4]^-$ or $[LHRe(CO)_4]$ intermediates, where L may be an oxo, μ-oxo or μ-hydroxo surface group. The reversible $[HRe_3(CO)_{14}]$–$[Re(CO)_3OH]_4$ transformation and the reaction of $[H_3Re_3(CO)_{12}]$ with CO to form $[HRe_3(CO)_{14}]$ on the surface are attributed to stabilization of rhenium intermediates by bonding to the silica, which hinders their reaction to form the volatile $[HRe(CO)_5]$. The formation of the monomeric intermediates may also result from the fragmentation of $[H_4Re_4(CO)_{12}]$ on silica; these intermediates evidently react with adsorbed water to form $[Re(CO)_3OH]_4$. This complex is the predominant organometallic species on the surface during catalysis of propene metathesis. The catalytically active species are a small fraction of the surface rhenium, inferred to be mononuclear complexes of the metal in an intermediate oxidation state. The high stability of the catalyst is associated with the near absence of alkene polymerization and coke formation, which are associated with rhenium in high oxidation states.[31,33,34]

Experimental Section

Synthesis. The precursor $[H_4Re_4(CO)_{12}]$ was prepared from $[Re_2(CO)_{10}]$ (Strem) by a modified literature method;[24] a reaction temperature of 175 °C was employed followed by refluxing under nitrogen for 0.5 h. All solvents were Fisher reagent grade. Benzene was further dried and redistilled before use. The observed infrared spectrum (in cyclohexane, 2042 and 1989 cm^{-1}) and ^1H NMR spectrum (in CCl_4, δ – 5.1) are in close agreement with those reported[24] for $[H_4Re_4(CO)_{12}]$.

The $[H_4Re_4(CO)_{12}]$ in a refluxing solution of *n*-octane (Fisher, reagent grade) was brought in contact with silica (Cabosil grade MS-5, surface area = 325 m^2 g^{-1}) for 4 h. In the standard preparation, the silica support was pretreated by slurrying with distilled water, followed by drying at 150 °C and then calcination at 400 °C (12 h) under vacuum (10^{-4} torr). The *n*-octane had not been dried, and the impurity water partially rehydrated the silica surface.[13] After the reaction mixture had cooled, the octane was decanted and the solid washed with cold CH_2Cl_2 to remove any physisorbed material and excess solvent. Uptake of rhenium by the solid varied from 65 to 95%, as determined by X-ray fluorescence spectroscopy of the solid; a maximum rhenium content of 3.43 wt % would have been achieved by complete uptake. The resulting cream-colored powder was then dried under vacuum (10^{-4} torr) for 12 h and transferred to a drybox for storage. Other preparations were carried out in which the calcination temperature of the support and the water content of the *n*-octane (distilled from Na) were varied.

A blank experiment was performed in which a *n*-octane solution of $[H_4Re_4(CO)_{12}]$ was refluxed with distilled water. The octane was decanted and the water layer subjected to the same procedure as that used previously[15] to recover $[Re(CO)_3OH]_4$ from an aqueous solution.

The complex $[Re(CO)_3OH]_4$ was also supported directly on silica. The compound was synthesized by the method of Herberhold et al.[15] The infrared band pattern of the compound in THF (2026, 1921 cm^{-1}) and the chemical shift in acetone-d_6 (δ 6.1) agree with the literature values.[15] The $[Re(CO)_3OH]_4$ was supported on the silica surface by the same method employed with $[H_4Re_4(CO)_{12}]$. Complete uptake of rhenium by the solid was observed (3.24 wt % Re) by X-ray fluorescence analysis of the solid.

$[H_3Re_3(CO)_{12}]$ was synthesized by the method of Huggins et al.[36] The infrared spectrum in cyclohexane (2094 m, 2084 w, 2030 vs, 2018 w, 2008 s, 1983 m, 1948 vw cm^{-1}) and UV–visible spectrum (255, 303, 345 nm) are in agreement with reported values.[20] The $[H_3Re_3(CO)_{12}]$ was physisorbed on silica by bringing a hexane solution of $[H_3Re_3(CO)_{12}]$ in contact with the solid for 4 h in a drybox. The solid was removed from the hexane by filtration and dried under vacuum (10^{-4} torr) for 4 h before use. X-ray fluorescence spectroscopy of the solid indicated a metal loading of 1.5 wt % Re.

Characterization of Supported Catalysts. A battery of spectroscopic techniques was applied to characterize the supported rhenium. Surface species and those extracted from the solid were characterized with infrared, electronic absorption (UV–visible), and ^1H NMR spectroscopies. X-ray photoelectron (XP) and X-ray fluorescence spectroscopies were also applied to some of the solid samples.

In situ infrared experiments were conducted to evaluate the stability and reactivity of the $[H_4Re_4(CO)_{12}]$- and $[H_3Re_3(CO)_{12}]$-derived surface species. Samples consisted of thin wafers (pressed at 686 atm) mounted in a quartz sample cell having NaCl windows and interfaced to a gas-handling system.[2] Sample preparation and loading of the cell were carried out in a drybox with the vigorous exclusion of air. Spectra were measured with a Nicolet 7199 Fourier transform infrared spectrophotometer. To improve the quality of the spectra (with the exception of the $[H_4Re_4(CO)_{12}]$-derived sample), the wafers (1 cm in diameter) were prepared by diluting the supported material (0.015 g) with pure silica (0.045 g). All spectra were obtained at 2-cm^{-1} resolution.

The stability of the surface complex derived from $[H_4Re_4(CO)_{12}]$ was evaluated by heating the sample under flowing helium (Matheson UHP grade, 99.995%) or vacuum and monitoring the infrared absorptions of the supported species. XP spectra of the solid were recorded before and after thermal treatment. Samples were briefly exposed to air (~1 min) while being loaded into the spectrometer.[37] The XP spectra were measured with pressed wafers and a Physical Electronics AES/XPS instrument (Model 550) equipped with a Mg source and a cylindrical mirror analyzer. Corrections for sample charging were made, and reported binding energies are referenced to the C_{1s} peak at 284.6 eV. The reactivity of the surface-bound metal carbonyl with CO (Airco grade 2.3, 99.3%) and with propene was investigated by monitoring the changes in the infrared spectrum.

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(34) It has been reported that the termination reaction leading to catalyst deactivation is stereospecific.[35] The surface may be acting as a bulky ligand to inhibit this reaction and thereby enhance stability.

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Extraction of supported organometallics with various solvents was carried out as about 30 mg of solid were added to 3 mL of solvent. The suspensions were allowed to stand in a drybox, and liquid samples were withdrawn periodically for infrared analysis. All samples were filtered before being placed in the infrared cell (0.202-mm path length).

Solid-state and solution ^{1}H NMR spectra of supported rhenium species were obtained with a spectrometer operated at a frequency of 56.41 MHz for the proton resonance. An extract of the surface species was prepared by bringing 40 mg of solid in contact with 0.4 mL of methanol-d_4 (distilled from magnesium turnings under N_2) for 0.5 h. A silica blank was also characterized. The magnet had an external deuterium lock to minimize field drift (<0.2 ppm). The solution and solid-state spectra were analyzed by coaddition of 50 and 1000 transients, respectively, followed by Fourier transformation.

Electronic absorption spectra of $[Re(CO)_3OH]_4$ in THF and of THF extracts of supported carbonyls were recorded with a Cary 219 spectrophotometer. UV-visible spectra of the solids were measured with a diffuse reflectance sphere (Model 40513); the cell path length was 1 mm. For the quantitative analysis of the extracts, 10 standards were run at λ_{max}; a linear regression coefficient of 0.99 was obtained.

The rhenium contents of the solids were evaluated with X-ray fluorescence spectroscopy by using a Phillips automated X-ray spectrometer (PW 1410/80) equipped with an XRG-3100 generator. Separately, solid samples were analyzed for Re by Schwarzkopf Microanalytical Laboratories, Woodside, NY, the results confirming those determined by X-ray fluorescence.

Catalytic Metathesis of Propene. The catalytic reaction experiments were carried out with solid samples of supported rhenium in a microflow reactor interfaced to a gas chromatograph (GC) (Antek 300). The flow system allowed monitoring of the propene and helium fed to a Pyrex reactor enclosed in a Lindberg furnace. The propene was Matheson CP grade (99.0%); propane (0.388%) was the sole impurity detected by GC. All gases flowed through traps to remove traces of oxygen (activated Cu) or water (Zeolite 5A). The reactor temperature was controlled with a Thermoelectric (Model 3813011128) proportional controller. At the beginning of each catalysis experiment, the reactor was loaded under nitrogen with 50–100 mg of catalyst powder dispersed between two layers of glass wool. The reactor was placed in the flow system (~1 min exposure to air) and purged with helium (0.25 cm^3/h) at 25 °C. The catalyst was then brought to temperature in flowing He. In one set of experiments, sample I (Table II) was heated to 150 °C within 5 min, the propene was then introduced at 0.15 cm^3/h, and the He flow was reduced to 0.10 cm^3/h to maintain a constant contact time. The catalyst was then treated with alternating periods of propene + He and He until steady state was attained, as indicated by the on-line product analysis.

A second set of experiments was performed with sample II (Table II), which was simply sample I pretreated at 250 °C in flowing He at 0.25 cm^3/h for 12 h. The temperature was then reduced to 150 °C and the reactant introduced. This set of experiments was also conducted with alternating propene + He and He feed. Omitting the periods of He flow resulted in a more rapid deactivation of the catalyst. Raising the reaction temperature also increased the deactivation rate.

During a catalysis experiment, the reactor effluent stream was periodically analyzed by GC. The product samples were separated in 3.18 mm × 10 m Supelco SP1700 column with a pressure drop of 7.8 atm. at 25 °C. The GC was equipped with a flame ionization detector; the response was calibrated for C_1–C_6 hydrocarbons. Products were identified by their retention times. To obtain reaction rates directly, differential conversions of propene (<1%) were measured.

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Registry No. $[Re(CO)_3OH]_4$, 56553-73-2; $[H_4Re_4(CO)_{12}]$, 60146-15-8.

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Isolation of Ionic Products in the Reaction of CO_2 with (Tetrahydroborato)copper(I) Complexes: Synthesis and Reactions of $[(biL)(Ph_3P)_2Cu][HB(O_2CH)_3]$ and $[(biL)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (biL = 1,10-Phenanthroline, 3,4,7,8-Tetramethyl-1,10-phenanthroline)

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Carbon dioxide reacts with the (tetrahydroborato)copper(I) complexes $(biL)(Ph_3P)Cu(BH_4)$ (biL = 1,10-phenanthroline (phen) (**1**), 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) (**2**)) in the presence of free triphenylphosphine. In nonprotic solvents the stable crystalline complexes of formula $[(biL)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (biL = phen (**3**)) and $[(biL)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (biL = phen (**4a**), TMP (**4b**)) can be isolated. The related reactions of **1** with $^{13}CO_2$ give the corresponding ^{13}C-labeled products; the reaction of $(TMP)(Ph_3P)Cu(BD_4)$ with CO_2 leads to the deuterated derivatives. In protic solvents, CO_2 reacts with **1** or **2**, allowing the isolation of the covalent formato complexes $(biL)(Ph_3P)Cu(O_2CH)$ (biL = phen (**5a**), TMP (**5b**)). These can be also obtained by heating **3**, **4a**, and **4b** in ethanol, suggesting that these ionic formato–hydroborato species probably act as intermediates in the reducing property of BH_4 toward carbon dioxide. The reactions of **4b** with HBF_4 and $NaBPh_4$ give the ionic derivatives $[(TMP)(Ph_3P)_2Cu](BF_4)$ and $[(TMP)(Ph_3P)_2Cu](BPh_4)$. Complexes **3** and **4a** have been confirmed to undergo a reversible interconversion. Infrared and multinuclear magnetic resonance data (^{1}H, ^{11}B, and ^{13}C) strongly support the presence of the $[HB(O_2CH)_3]^-$ and $[H_2B(O_2CH)_2]^-$ anions in the complexes **3**, **4a**, and **4b**. In particular their ^{11}B NMR spectra substantiate the existence of the BH and BH_2 groups in these ionic products.

Introduction

Covalent metal tetrahydroborato complexes have received increasing attention in recent years. An excellent comprehensive review of this topic has been published in 1977, including a discussion of reasons for the interest in these compounds.[1] Despite the large number of known tetrahydroborato complexes,[2-5] only a few papers have been published dealing with their reactivity. The facile reduction of carbon dioxide and other CO_2-like hetercallenes by copper(I) tetrahydroborato complexes containing only tertiary phosphines as ligands has been reported.[6] In all

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